

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



REC'D 02 FEB 2005

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Applicant's or agent's file reference 032628wo	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 03/13221	International filing date ( <i>day/month/year</i> ) 25.11.2003	Priority date ( <i>day/month/year</i> ) 29.11.2002
International Patent Classification (IPC) or both national classification and IPC C08G63/85		
Applicant CROMPTON GMBH et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.  
  
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
  
 These annexes consist of a total of 9 sheets.

3. This report contains indications relating to the following items:
  - I ☒ Basis of the opinion
  - II ☐ Priority
  - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV ☐ Lack of unity of invention
  - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☐ Certain documents cited
  - VII ☐ Certain defects in the international application
  - VIII ☐ Certain observations on the international application

Date of submission of the demand  05.05.2004	Date of completion of this report  31.01.2005
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Kaul-Buchberger, E  Telephone No. +49 89 2399-8296  

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP 03/13221

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-14, 18-22, 25-37	as originally filed
15-17, 23, 24, 24a	received on 27.08.2004 with letter of 25.08.2004

**Claims, Numbers**

1-17	received on 25.08.2004 with letter of 23.08.2004
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
  - ☐ the language of publication of the international application (under Rule 48.3(b)).
  - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
  - ☐ filed together with the international application in computer readable form.
  - ☐ furnished subsequently to this Authority in written form.
  - ☐ furnished subsequently to this Authority in computer readable form.
  - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/13221**

**III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application,

☒ claims Nos. 5-7

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 5-7 are so unclear that no meaningful opinion could be formed (*specify*):

**see separate sheet**

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the Standard.

☐ the computer readable form has not been furnished or does not comply with the Standard.

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	9-11,13-15
	No: Claims	1-4,8,12,16,17
Inventive step (IS)	Yes: Claims	9-11,13-15
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-17
	No: Claims	

2. Citations and explanations

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/13221

**Re Item III**

**Clarity**

- 1.1. The catalytic compositions of claims 1-4, which are defined by the general formula (I) cannot be prepared by reacting the compounds defined in said formula (I) with a metal alcoholate as claimed in claims 5-7.
- 1.2. Therefore, the subject-matter of claims 5-7 is unclear and does not meet the requirements of Article 6 PCT.

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. The combination of the features A<sup>+</sup>, which is a chloride and R1, which is an octyl group is not disclosed in the application as originally filed and, thus, claim 4 does not meet the requirements of Article 19(2) PCT.
2. Reference is made to the following documents:  
  
D1 = US-A-6114496  
D2 = EP-A-0419254  
D3 = US-A-4014858  
D4 = US-A-5663281  
D5 = S. Durand, K. Sakamoto, T. Fukuyama, A. Orita, A. Duthie, D. Dakternieks, M. Schulte, K. Jurkschat, Organometallics 2000, 19, 3220-3223  
D6 = H. Puff, H. Reuter, J. of Organometallic Chemistry, 373 (1989), 173-184
- 3.1. Document D5 discloses (pages 3220 and 3221, examples 8-12) a catalytic composition containing  $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}\text{Cl}^-_2 \cdot 2\text{H}_2\text{O}$  for the acetylation of 2-Phenylethanol.
- 3.2. Due to the fact that claims 1-4 define the tin compounds as such, which are not limited to the use (for esterification, transesterification,...) , the subject-matter of claims 1-4 lacks novelty in view of D5.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/13221

Hence, the reaction defined in D5 represents an esterification, the subject-matter of claim 8 and 12 lacks novelty in view of D5.

- 3.3. Document D6 discloses (page 173)  $[(\text{I-PrSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ .
- 3.4. Due to the fact that claims 1-4 define the tin compounds as such, which are not limited to the use (for esterification, transesterification,...) , the subject-matter of claims 1-3 lacks novelty in view of D6.
- 3.5. There exists no structural difference between the polyesters defined in claims 16 and 17 and known polyesters (e.g. PET, PBT,...) and, thus, the subject-matter of said claims lacks novelty in view of said polyesters.
- 4.1. Documents D1-D4 are regarded as the most relevant prior art for the assessment of inventive step of use claims 9-11 and 13-15, wherein the  $\text{Sn}_{12}$  cluster compounds are used as catalyst. Said documents disclose polyesterification and polytransesterification in the presence of another organic tin catalyst.
- 4.2. The examples show that the catalysts according to the invention show a higher polycondensation rate than a usual organo tin compound (monobutylstannic acid).
- 4.3. The cited literature does not suggest this effect and, thus, the subject-matter of claims 9-11 and 13-15 fulfill the requirements of Article 33(3) PCT.
- 5.1. In process claim 6 the basis for the proportion of metal alkoxide is not defined and, thus, said claim is unclear and does not meet the requirements of Article 6 PCT.
- 5.2. A linear, branched or cyclic alkyl group is not an anion as defined in claim 2 and, thus, said claim is unclear and does not meet the requirements of Article 6 PCT. On page 7, lines 7-11 the correct definition is given.
6. For all claims (1-17) industrial applicability is acknowledged.

# Druckexemplar

Further alkyltin catalysts:

Comparative Example 1g (Tributyltin (2-ethylhexanoate):

- 5 A three-necked flask equipped with mechanical mixer, heating, thermometer and vacuum distillation bridge was, under nitrogen protective atmosphere, filled with 149 g (0,25 Mol) hexabutyldistannoxane and 72,1 g (0,5 Mol) 2-ethylhexanoic acid. The reaction mixture was heated up on 80°C. To separate from the reaction water a vacuum of 1  
10 mbar was applied, and the reaction mixture was stirred another 1 h at this temperature.

Yield: 209,8 g (theoretical. 212,1 g) a clear, bright liquid.

Elemental analysis: Sn content = 27,8 %.

- 15 The production of the examples and comparative examples 1h to 1n followed the same procedure.

Comparative example 1h: Dibutyltin bis(2-ethylhexanoate)

- 20 Comparative example 1i: monobutyltin tris(2-ethylhexanoate)

Comparative example 1j: dibutyltin pinacolate

Comparative example 1k: monooctylstannoic acid

25

Comparative example 1l: monobutylstannoic acid

Comparative example 1m: monooctyltin tris(2-ethylhexanoate)

Comparative example 1n: monododecyltin tris(2-ethylhexanoate)

Example 2: Catalyst test by synthesis of a resin for powder coatings:

5 Starting materials, quantitles:

terephthalic acid                      83,07 g                      [0,50 mol]

10 neopentyl glycol                      (2,2-dimethyl-1,3-propandiol)  
104,15 g                      [1,00 mol]

catalyst:                      0,05 % [m/m] (as metal)

Synthesis:

15 Catalyst, neopentyl glycol and terephthalic acid were given into a 250 ml  
three necked round bottom flask. The mixture was heated to a maximum  
by the means of a heating mantel and the reaction water was distilled off  
and the amount was measured.

20 The reaction time equals the time between the first water formation and  
the "clear point" of the reaction.

25 Table 1 shows the acceleration of the reaction time in the described resin  
synthesis with the mixtures of examples 1a, 1b, 1c, 1d, 1e, 1f in  
comparison with the uncatalyzed reaction or with monobutyltin oxide  
(0,05 % [m/m]) as catalyst.

Table 1: Reaction time of the mixtures a-f in comparison.

	Volume H <sub>2</sub> O [ml]:												[min]	
Catalyst (0,05% as Sn)	15 min	30 min	45 min	60 min	75 min	90 min	105 min	120 min	135 min	150 min	165 min	180 min	Reac- tion time	Remarks
Without catalyst				1		1		2		3		4	300	aborted
monobutyl- tin oxide		7		9		12		15		17		19	180	Clear, colorless
1a		7		10		18							90	Clear, colorless
1b	3	6	5	9	11	14							90	hazy, colorless
1c	4	4	10	14	16								75	Clear, colorless
1d	3	6	10	12	14	16							90	Clear, colorless
1e	3	5	6	8	9	10	13	15	18				135	Clear, colorless
1f	3	5	7	10	12	14	15	16	18				135	Clear, colorless

5 Example 3: Catalytically active Sn-compounds with A = alcoholate:

Example 3o: Product of the reaction of monobutyl stannic acid with Ti(Obu)<sub>4</sub> (molar ratio 4 : 1):

- 10 51,1 g (0,15 mol) Ti(Obu)<sub>4</sub> and 25.3 g (0,60 mol) monobutyl stannic acid were dissolved in xylene (250 ml) and refluxed under a nitrogen atmosphere in a 500 ml three necked round bottom flask for 4 hours. The product was obtained after the solvent was removed under reduced pressure in an amount of 149,6 g (theoretical. 131,9 g) as a yellow solid
- 15 (Elemental analysis: Sn content = 46,5 %, Ti content = 4,9 %).



Table 3. Polycondensation of BHET with Sb and Ti catalysts.

catalyst	temperature [°C]	time [min]	catalyst conc. [ppm]	P <sub>n</sub>
antimony triacetate	270	30	190	25
antimony triacetate	270	60	190	45
antimony triacetate	270	90	190	65
antimony triacetate	270	120	190	85
antimony triacetate	270	150	190	100
antimony triacetate	270	180	190	115
antimony triacetate	280	30	190	30
antimony triacetate	280	60	190	55
antimony triacetate	280	90	190	75
antimony triacetate	280	120	190	95
antimony triacetate	280	150	190	115
antimony triacetate	280	180	190	135
tetrabutyl titanate	280	30	20	45
tetrabutyl titanate	280	60	20	65
tetrabutyl titanate	280	90	20	85
tetrabutyl titanate	280	120	20	105
tetrabutyl titanate	280	150	20	125
tetrabutyl titanate	280	180	20	150

Further polycondensation reactions starting from bis-(2-hydroxyethyl)-terephthalate (BHET) were carried out in the glass equipment with screw mixer in presence of the catalysts 1 until 12.

- Catalyst of comparative example 1g : tributyltin (2-ethylhexanoate)
- Catalyst of comparative example 1h: dibutyltin bis(2-ethylhexanoate)
- Catalyst of comparative example 1i: monobutyltin tris (2-ethylhexanoate)
- Catalyst of comparative example 1j: dibutyltin pinacolate
- Catalyst of comparative example 1k: monooctylstannoic acid

- Catalyst of comparative example 1l: monobutylstannoic acid
  - Catalyst of comparative example 1m: monooctyltin tris(2-ethylhexanoate)
  - Catalyst of comparative example 1n: monododecyltin tris(2-ethylhexanoate)
  - Catalyst of example 3o: conversion product from monobutylstannoic acid with tetrabutyl titanate (4 Mol : 1 Mol)
  - Catalyst of example 3p: conversion product from monooctylstannoic acid with tetrabutyl titanate (1 Mol : 1 Mol)
  - Catalyst of example 3q: conversion product from monooctylstannoic acid with tetrabutyl titanate (4 Mol : 1 Mol)
  - Catalyst of example 3r: conversion product from monobutylstannoic acid with tetrabutyl titanate (2 Mol : 1 Mol)
- For the determination of the catalyst activity at first two concentrations of 20 ppm and 100 ppm were compared. The catalysts of (comparative) examples 1g through 1j were dissolved in toluene.

The catalysts were dissolved in dry toluene. The neat tin catalysts were used at a catalyst concentration of 40 ppm. The mixed catalysts (catalyst of examples 3o through 3q) were used at a tin content of 20 ppm. For the catalyst of example 3r the tin content of the catalyst was 22.9 ppm.

The tables 4a and 4b show the tin content and dosed catalyst amounts of the respective experiments.

BHET and the catalyst were introduced into the reaction vessel and rinsed well with nitrogen.

- 24 a-

The reaction vessel was placed into the salt bath. Recording of reaction time started now. Within 15 min the pressure was lowered from 100

5

10

Druckexemplar

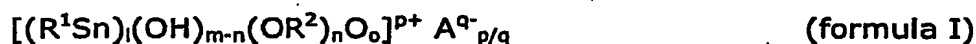
PCT/EP03/13221  
Crompton GmbH

HPJ/RC/cr

23 August 2004

## C L A I M S

1. Catalytic composition for esterification, transesterification and polycondensation reactions of dicarboxylic acids, polycarboxylic acids and/or hydroxy carboxylic acids and alcohols containing tin compounds of the general formula (I):



wherein:

$R^1$  and  $R^2$  each independently is a linear, branched or cyclic alkyl group or aryl group having 1 to 12 carbon atoms,

$A^{q-}$  is an anion,

$l = 12$ ,

$m = 6$ ,

$n = 0$  to  $6$ ,

$o = 14$ ,

$p = 2$  and

$q = 2$ .

2. Catalytic composition according to claim 1, characterized in that the anion  $A^{q-}$  is  $O^{2-}$ ,  $-OH^-$ , a linear, branched or cyclic alkyl group, aryl carboxy group or alkoxy group each having 1 to 12 carbon atoms, the anion of a mineral acid or a metalate.

3. Catalytic composition according to claim 2 characterized in that the anion  $A^{q-}$  is a sulphate, sulphite, phosphate, halogenide or pseudo-halogenide, titanate, zirconate, aluminate or zincate anion.

- 6 -

4. Catalytic composition according to claim 1 characterized in that the anion  $A^{n-}$  is a chloride anion and R1 is an octyl- and/or butyl group.
5. Process for the preparation of a catalytic composition according to any one of claims 1 to 4 wherein  $n = 1$  to 6 characterized by reacting tin compounds of the general formula (I) as to the definition in claim 1 with a metal alcoholate.
6. Process according to claim 5, characterized by using said metal alkoxide in a proportion of 1:0.0001 up to 1:20 by mole, in particular 1 : 4 to 1 : 6.
7. Process according to claim 7 or 8 characterized in that the resultant metal oxides, metal hydroxides and /or alkoxy metal hydroxides remain in the catalytic composition.
8. Use of the catalytic composition as defined in any one of claims 1 to 7 for the continuous or batchwise production of esters or polycondensation products by esterification, transesterification, polyesterification or polytransesterification reaction.
9. Use according to claim 7 including a polyesterification reaction of a dicarboxylic acid derivative with a mono, divalent or polyvalent alcohol.
10. Use according to any one of claims 7 to 9, characterized by employing derivatives of di, or polycarboxylic acids being selected from the group of esters or halogenides.
11. Use according to claims 7 to 10, characterized by employing derivatives of hydroxycarboxylic acids being selected from esters.

- 7 -

12. Use according to anyone of claim 7 to 11, characterized by employing a metal concentration of said catalytic composition being in the range of 0.1 ppm to 1 mole-%, in particular 10-100 ppm with reference to the acid or derivative to be reacted.

13. Use according to any one of claims 7 to 12, characterized by employing a solvent or suspending agent for the manufacturing of the catalytic composition and/or said esterification, transesterification, polyesterification or polytransesterification reaction.

14. Use according to claim 13, characterized by employing the same solvent and/or suspending agent the manufacturing of said catalytic composition and said esterification, transesterification, polyesterification or polytransesterification reaction.

15. Use according to claim 13 or 14, characterized by employing a solvent or suspending agent being selected from the group of mono-, di- or polyvalent alcohols being reacted in said esterification, transesterification, polyesterification or polytransesterification reaction.

16. Polyester for bottles, films, folls, yarn and/or molded padding, or resins for powder coatings or technical synthetic materials, obtainable by a process employing a catalytic composition as defined in any one of claims 1 to 4 in a use according to any one of claims 8 to 15.

17. Polyester or resins according to claim 16, wherein said polyester is selected from the group of polyethylene terephthalate, poly-2,2-dimethylpropyl-1,3-terephthalate, polypropylene terephthalate, polydiethyleneglycol terephthalate, polybutylene terephthalate, polynaphthalene terephthalate, or polyethylene naphthalate.